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## (54) SINTERED PERMANENT MAGNET

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To improve corrosion resistance by making the main phase crystal particle diameters of a magnet to be not more than a specified value in the R-Fe-B system sintered permanent magnet with rare earth and oxygen of the specified range amounts.

**SOLUTION:** In the sintered permanent magnet, composition where R (R is one type or more than two types of rare earth elements containing Y) is 28.0–33.0%, B is 0.5–2.0%, O is 0.3–0.7% and a remaining part is Fe at a weight percentage is provided, and the sum of the areas of main phase crystal particles whose crystal particle diameters are not more than 10 $\mu\text{m}$  is not more than 10% against the total area of the magnetic main phase. In the sintered permanent magnet, a part of Fe is substituted for one type or more than two types among Nb 0.1–2.0%, Al 0.02–2.0%, Co 0.3–5.0%, Ga 0.01–0.5% and Cu 0.01–1.0 or the value of coercive force iHc is made to be not less than 13.0kOe. Thus, the R-Fe-B system sintered permanent magnet having superior corrosion resistance can be obtained without deteriorating a magnetic characteristic.

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(54)【発明の名称】 焼結型永久磁石

(57)【要約】

【課題】 本発明は、R-Fe-B系焼結型永久磁石の磁気特性を低下させずに、耐蝕性を改善することを目的とする。

【解決手段】 重量百分率でR(RはYを含む希土類元素のうちの1種又は2種以上)28.0~33.0%, B 0.5~2.0%, 0.3~0.7%, 残部Feの組成を有し、磁石主相結晶粒の総面積に対し、結晶粒径が10μm以下の主相結晶粒の面積の和が80%以上、結晶粒が13μm以上の主相結晶粒の面積の和が10%以下である焼結型永久磁石。

## 【特許請求の範囲】

【請求項 1】 重量百分率でR(RはYを含む希土類元素のうちの1種又は2種以上)28.0~33.0%, B 0.5~2.0%, 0.3~0.7%, 残部Feの組成を有し、磁石主相結晶粒の総面積に対し、結晶粒径が $10\mu\text{m}$ 以下の主相結晶粒の面積の和が80%以上、結晶粒が $13\mu\text{m}$ 以上の主相結晶粒の面積の和が10%以下であることを特徴とする焼結型永久磁石。

【請求項 2】 Feの一部をNb 0.1~2.0%, Al 0.02~2.0%, Co 0.3~5.0%, Ga 0.01~0.5%, Cu 0.01~1.0%のうち1種または2種以上で置換する請求項1に記載の焼結型永久磁石。

【請求項 3】 保磁力*iHc*の値が13.0kOe以上である請求項1または2に記載の焼結型永久磁石。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、R-Fe-B系の希土類磁石の性能改善に関するものである。

## 【0002】

【従来の技術】 焼結型希土類永久磁石の中でR-Fe-B系(RはYを含む希土類元素のうちの1種又は2種以上)焼結型永久磁石は高性能磁石として注目され、広い分野で使用されている。このR-Fe-B系焼結型永久磁石は、基本的にはR2Fe14B相(主相)、RFe7B6相(Brich相)、R85Fe15相(Rrich相)の3相から成る構造を有している。組成的に希土類元素に豊んだRrich相の存在と、このような3相構造に由来して、R-Fe-B系焼結型永久磁石はSm-Co系焼結型永久磁石に比べて耐蝕性が劣り、この永久磁石の開発当初から現在に至るまで欠点の1つとなっている。R-Fe-B系焼結型永久磁石の腐蝕のメカニズムについての定説は無いが、Rrich相を起点とした腐蝕の形態が一般的であることから、Rrich相を陽極とした陽極腐蝕との見方もある。確かに、R-Fe-B系焼結型永久磁石の希土類元素の量を減少することによって、その焼結体内部のRrich相の量は減少し、かつ相の形態は微細化し、これに対応して永久磁石の耐蝕性は向上する。従って、希土類元素の量を減少することは、R-Fe-B系焼結型永久磁石の耐蝕性改善の一つの方法である。

【0003】 R-Fe-B系を含む焼結型の希土類永久磁石は、原料金属を溶解し鋳型に注湯して得られたインゴットを粉碎、成形、焼結、熱処理、加工するという粉末冶金的な工程によって製造されるのが一般的である。しかし、インゴットを粉碎して得られる合金粉末は、希土類元素を多量に含むため化学的に非常に活性であり、大気中において酸化して含有酸素量が増加する。これによって、焼結後の焼結体では希土類元素の一部が酸化物を形成し、磁気的に有効な希土類元素が減少する。このため、実用的な磁気特性の水準、例えば*iHc* $\geq 13\text{kOe}$ を実現するためには、R-Fe-B系焼結型永久磁石の希土類元素の量を増やす必要があり、重量百分比率で31%を越える希

土類元素の添加量が実用材料では採用されている。このため、これまでのR-Fe-B系焼結型永久磁石の耐蝕性は十分ではなかった。

## 【0004】

【発明が解決しようとする課題】 本発明は、以上述べたR-Fe-B系焼結型永久磁石の耐蝕性を大幅に改善しようとするものである。

## 【0005】

【問題を解決するための手段】 本発明者らは、R-Fe-B系焼結型永久磁石の耐蝕性を改善するため種々検討した結果、特定範囲量の希土類量と酸素量のR-Fe-B系焼結型永久磁石において、その磁石主相結晶粒径を特定値以下とすることによって、耐蝕性が向上することを見い出して本発明に至ったものである。

【0006】 以下、本発明を具体的に説明する。本発明における焼結型永久磁石は、重量百分率でR(RはYを含む希土類元素のうちの1種又は2種以上)28.0~33.0%, B 0.5~2.0%, 0.3~0.7%, 残部Feの組成を有し、磁石主相の総面積に対し、結晶粒径が $10\mu\text{m}$ 以下の主相結晶粒

の面積の和が80%以上、結晶粒径が $13\mu\text{m}$ 以上の主相結晶粒の面積の和が10%以下であることを特徴とする。また、本発明焼結型永久磁石において、Feの一部をNb 0.1~2.0%, Al 0.02~2.0%, Co 0.3~5.0%, Ga 0.01~0.5%, Cu 0.01~1.0%のうち1種または2種以上で置換することができる。

【0007】 本発明者らは、上記組成を有するR-Fe-B系焼結型永久磁石の耐蝕性に結晶粒径依存性があり、磁石主相結晶粒径を特定値以下にすることによって、特に優れた耐蝕性が発現されることを見い出した。磁石結晶粒

径の定義と測定には種々の方法があり得、一義的ではないが、発明者らは磁石主相の総面積に対する粒径が一定寸法以下の主相結晶粒の面積の和の割合と、同じく磁石主相の総面積に対する粒径が一定寸法以上の主相結晶粒の面積の和の割合によって、磁石結晶粒径の状態を示す尺度とした。以下この尺度を用いて本発明の効果を説明することとする。また、この割合を算出するに当たっての計測は、対象とするR-Fe-B系焼結型永久磁石の結晶組織を、OLYMPUS社製顕微鏡(商品名VANOX)で観察し、この画像をNIRECO社製画像処理装置(商品名LUZEX 2)に直接

40 投入して行った。

【0008】 本発明者らは、特許請求範囲に示す組成を有するR-Fe-B系焼結型永久磁石の主相結晶粒径と耐蝕性の関係について下記の様な評価を行い、図1に示すような結果を得た。図1は、磁石主相結晶の総面積に対する、結晶粒径が $10\mu\text{m}$ 以下の主相結晶粒の面積の和の割合と、同じく磁石主相結晶の総面積に対する結晶粒径が $13\mu\text{m}$ 以上の主相の結晶粒の面積の和の割合と、耐蝕性的加速試験での、Niメッキのハクリ開始が生じるまでの経過的間との関係を示したものである。○印は重量百分比でNd 22.8%, Pr 6.7%, Dy 2.0%, B 1.0%, Al 1.0

%、C 0.45%、C 0.08%、N 0.015%、残部Feの組成を有する焼結体、□印は重量百分比率でNd 31.0%、Dy 1.0%、B 1.05%、Al 0.05%、Co 2.0%、Ga 0.09%、O 0.55%、C 0.07%、N 0.008%、残部Feの組成を有する焼結体、△印は重量百分比率でNd 23.0%、Pr 5.0%、Dy 4.5%、B 1.1%、Nb 1.0%、Al 0.2%、Co 2.0%、Cu 0.08%、O 0.35%、C 0.06%、N 0.030%、残部Feの組成を有する焼結体を示す。この場合の加速試験では、磁石を10mm×10mm×2mmの寸法に加工後、その表面に15μmのNiメッキを施し、次いで試料を2気圧、120°C、湿度100%の条件に放置した。図1から、磁石主相の結晶の総面積に対し、結晶粒径が10μm以下の主相結晶粒の面積の和が80%以上で、かつ結晶粒径が13μm以上の主相結晶粒の面積の和が10%以下である場合において、特許請求範囲に示す組成を有するR-Fe-B系焼結型永久磁石の耐食性が特に優れたものになることがわかる。従って、磁石主相結晶粒の大きさは、上記に規定される。

【0009】この原因を推定すると、比較的大きな主相結晶粒が存在する永久磁石焼結体においては、相対的に主相結晶粒の間の空隙部、具体的には粒界3重点がその種たる部分であり、ここには極めて酸化されやすいNd-rich相が存在しているが、このNd-rich相で充填されている空隙部の体積が大きくなる。腐食破壊をもたらす因子、例えば本加速試験では水分であるが、この様な因子の浸透性が良く、結晶粒界の破壊が連鎖反応的に起こりやすい状態にあるものと考えられる。以上は、特許請求の範囲に示す組成を有するR-Fe-B系焼結型永久磁石の耐食性に主相結晶粒径依存性があることを、本発明者等の研究結果の一例を示すことによって説明したものである。

【0010】特許請求範囲の組成を有するR-Fe-B系焼結型永久磁石の主相の結晶粒径を上記の規定範囲のものに制御する方法は必ずしも一義的ではなく、種々の方法あるいはそれらの方法の組合せによって達成することができるが、発明者らの研究では、通常の方法ではかなりの困難を伴う。一般に、R-Fe-B系焼結型永久磁石の製造においては、原料粗粉を微粉碎によって微粉化し、この微粉を磁界中で金型成形して成形体を得、これを焼結して焼結体とする方法が採られる。例えば、微粉碎をジェットミルを用いて行う場合には、粉碎時のガスの圧力や粗粉の供給速度等を制御することにより、所定の平均粒度や粒度分布を持つ微粉を得ることができる。また、必要に応じて、分級をおこなうことにより、微粉の粒度分布を制御することもできる。このようにして作製した微粉を成形し、焼結するにあたっては、さらに適切な焼結温度・時間・パターンを選択することによって、R-Fe-B系焼結型永久磁石の主相の結晶粒径を上記の規定範囲のものとすることは必ずしも不可能ではない。しかし、多くの条件を設定し、これを制御する必要があり、所定の結晶粒径を有する焼結体を再現性よく製造するのははなは

だ困難であることが判った。

【0011】本発明者らは特許請求範囲の組成を有するR-Fe-B系焼結型永久磁石の主相の結晶粒径を上記の規定範囲とするのに容易で量産上適した方法を探索した結果、いわゆるストリップキャスト法と呼ばれる方法で製造された所定の組成を有するR-Fe-B系急冷薄帯状合金を、所定の温度範囲で熱処理し、これを粉碎して原料粗粉とする方法を見い出した。また熱処理後の薄帯状合金を粉碎するにあたっては、水素吸蔵により自然崩壊させた後脱水素処理を施してから行うことが微粉碎性能を高めるうえで有効である。図2は、重量百分比率でNd 22.7%、Pr 7.6%、Dy 1.5%、B 1.05%、Al 0.05%、O 0.01%、N 0.004%、C 0.007%、残部Feの組成を有する、ストリップキャスト法で製造された薄帯状合金の断面組織である(as cast)。デンドライト状の微細な組織が存在している。写真の中で白色に観察される相は希土類量が少なく永久磁石焼結体の主相に相当する相、黒色に観察される相は希土類量が多い永久磁石焼結体のRich相に相当する相である。このRich相は微粉碎時に破壊の起点となるので、このRich相が図2に示すように微細に分散している帶状合金を使用した場合、粒径が細かくて均一な微粉が確率的に生成しやすい。従って、微粉碎時や焼結時の多くの条件を厳密に管理することなく、比較的容易にしかも再現性よく特許請求範囲の粒度分布を有する焼結体が製造可能となるのである。しかしこの薄帯状合金(急冷鋳造のまま)をこのまま直接粉碎して原料粗粉とし、これを微粉碎しても、良好な微粉の粒度分布は得られず、これを成形・焼結した焼結体では、本発明にかかる主相結晶粒径は得られない。この理由は、急冷鋳造によって薄帯状合金の表面が硬化し、微粉碎時の被粉碎性をいちじるしく悪化させるからである。

【0012】本発明者らは、この問題を解決する手段として、この薄帯状合金を特定温度範囲で熱処理して薄帯状合金表面の硬化を除去することが有効であることを見い出した。熱処理の温度は800°C～1100°Cとされる。これは、熱処理温度が800°C未満では硬化の除去が不十分だからである。また、1100°Cより高い温度では、熱処理時に薄帯状合金間で反応が生じ、後工程での処理に困難が生じるからである。活性な希土類元素を多量に含有する薄帯状合金であるため、熱処理は不活性ガス雰囲気中又は実質的な真空中で行う必要があることは言うまでもない。また、前記のように、熱処理後の薄帯状合金に水素を吸蔵させて自然崩壊させ、脱水素処理をおこなった後、これを粗粉化することは、微粉碎性を高めるうえでさらに有効である。これは、熱処理による薄帯状合金表面の硬化の除去効果に加え、水素による薄帯状合金内部の主にはRich相のせい化効果が加わることによる。

【0013】表1に、薄帯状合金を各種条件で熱処理(1Hr)あるいは粉碎して粗粉とし、これを同一条件で微粉碎し、成形・焼結した場合の焼結体の主相結晶粒径の状

態を示す。

【0014】

\* [表1]

\*

| 評価項目   |   | 薄体状合金熱処理<br>温度(℃) | 急冷鋳造<br>まま | 700       | 800  | 900  | 1000 | 1100 | 1200 |
|--------|---|-------------------|------------|-----------|------|------|------|------|------|
|        |   |                   |            | 10μ<br>以下 | 67   | 75   | 84   | 86   | 88   |
| 水素吸蔵なし | 主相結晶粒径<br>面積に対する<br>特定寸法の<br>主相結晶粒の<br>面積の和の<br>割合(%) | 13μ<br>以上         |            | 25        | 18   | 8    | 6    | 6    | 5    |
|        |   |                   |            |           |      |      |      |      | 5    |
| 水素吸蔵あり | 磁気特性  | Br (KG)           | 12.8       | 12.8      | 13.1 | 13.1 | 13.2 | 13.2 | 13.2 |
|        |   | iHc(kOe)          | 15.2       | 15.2      | 16.0 | 15.9 | 15.8 | 15.8 | 15.8 |
| 水素吸蔵あり | 主相結晶粒径<br>面積に対する<br>特定寸法の<br>主相結晶粒の<br>面積の和の<br>割合(%) | 10μ<br>以下(%)      | 73         | 77        | 88   | 90   | 84   | 95   | 85   |
|        |   | 13μ<br>以上(%)      |            | 18        | 13   | 6    | 4    | 3    | 2    |
| 水素吸蔵あり | 磁気特性  | Br (KG)           | 12.9       | 12.9      | 13.1 | 13.1 | 13.2 | 13.2 | 13.2 |
|        |   | iHc(kOe)          | 16.5       | 15.5      | 16.1 | 16.1 | 16.0 | 16.0 | 16.0 |

【0015】表1から、薄帯状合金を800℃以上の温度で熱処理し、これを用いることによって、特許請求範囲に示す主相粒径の割合を有する焼結体が得られることがわかる。また、前述したように、水素処理の有効性も明かである。同時に表1から、700℃での熱処理での主相粒径の状態は、急冷鋳造したものとほぼ同水準である。700℃の熱処理温度では、薄帯合金の表面硬化の除去に不十分であることがわかる。同時に本発明者らは、薄帯状合金の800℃以上の温度での熱処理が、磁気特性のうち特にBrの向上効果をもたらすことを見い出した。結果を同じく表1に示す。表1から、急冷鋳造状態と700℃の熱処理の薄帯状合金による永久磁石焼結体のBrは12.8~12.9KGであるが、800℃と900℃の熱処理の薄帯状合金を使用した場合には、Brは13.1KGと急激に増加する。熱処理温度が1000℃では、結果として得られるBrは微増し、13.2KGとなる。1100℃、1200℃の熱処理温度では、Brの増加は飽和に達し、13.2KGと変わらない。表1に示した薄体状合金のうち、急冷鋳造後の薄体状合金の金属組織写真を図2に、急冷鋳造後1000℃で熱処理した薄体状合金の金属組織写真を図3に示す。図2、図3を比較すると、熱処理により、薄体状合金内の主相に相当する白色組織、R rich相に相当する黒色組織のいずれもが粗大化していることがわかる。これらのことから本発明者等は、急冷鋳造のままの薄体状合金では主相およびR rich相に相当する相から構成される組織が微細であるために、これを用いて微粉を製造した場合、微粉の内に多結晶状態のままのものが確率的に多く存在し、微粉を磁界中で金型成形する際の配向性の低下を招き、永久磁石焼結体のBr低下をもたらしているものと考え

る。700℃の熱処理温度では、組織の成長が不十分で配向性の改善には至らない。熱処理温度の上昇にしたがって薄体状合金の内部組織が粗大化しているが、これによつて多結晶状態の微粉の発生の確率が低下し、Brが改善されると考えられるが、表1の結果から判断する限り、800℃の熱処理温度でその効果はかなりでているものと考えられる。薄体状合金の熱処理温度のさらなる増加にしたがつて、得られる焼結体のBrは向上するものの1000℃以上の熱処理温度では飽和の傾向を示す。これは、薄体状合金内部の組織がある程度粗大化し、多結晶状態の微粉が確率的にはほとんど発生しない状態に達した段階では、熱処理温度をさらに上げて組織の粗大化を促進させても、それは得られる焼結体のBrの向上として反映しないといふことで理解できる。

【0016】以上詳細に説明したように、ストリップキャスト法による所定の組成の急冷鋳造薄帯状合金を、特定の温度範囲において熱処理し、あるいはこれに水素吸蔵処理を施して自然崩壊させ、これを粉碎して粗粉化することによって、微粉碎時の粉碎度が改善され、これを用いて製造された永久磁石焼結体は、耐蝕性にきわめて優れた特許請求範囲に示した主相結晶粒径を有するものとなるのであるが、それのみならず、高い磁気特性を有するものにもなるのである。なお、薄帯状合金の800~1100℃での熱処理時間は、少なくとも15分以上好ましくは30分以上行う必要がある。

【0017】以下では、本発明のR-Fe-B系焼結型永久磁石の組成の限定理由を述べる。希土類元素の量は、重量百分率で28.0~33.0%とされる。希土類元素の量が31.0%を越えると、焼結体内部のRrich相の量が多くなり、

かつ形態も粗大化して耐蝕性が悪くなる。一方、希土類元素の量が28.0%未満であると、焼結体の緻密化に必要な液相量が不足して焼結体密度が低下し、同時に磁気特性のうち残留磁束密度Brと保磁力iHcが共に低下する。

従って、希土類元素の量は28.0~33.0%とされる。また、希土類元素の量を31.0%以上とすることにより、高い焼結体密度を有する焼結体を容易に得ることができる。0の量は重量百分率で0.3~0.7%とされる。0の量が0.7%を越える場合には、希土類元素の一部が酸化物を形成し、磁気的に有効な希土類元素が減少して保磁力iHcが低下する。一方、微粉碎工程での酸化によって、最終焼結体の0量を0.3%未満とすることは困難であり、0量は0.3~0.7%とする。

**【0018】**Cの量は重量百分率で0.15%以下とすることが好ましい。Cの量が0.15%より多い場合には、希土類元素の一部が炭化物を形成し、磁気的に有効な希土類元素が減少して保磁力iHcが低下する。C量は、0.12%以下とすることがより好ましく、0.10%以下とすることがさらに好ましい。一方、溶解によって作製するインゴットのC量の水準は最大0.008%であり、最終焼結体のC量をこの値以下とすることは困難であり、焼結体のC量は0.01~0.15%とすることが好ましい。Nの量は、重量百分率で0.002~0.04%とすることが好ましい。Nの量が0.04%を超えると、希土類元素の一部が窒化物を形成し磁気的に有効な希土類元素が減少して保磁力iHcが低下する。また、微粉碎の過程で若干の窒化を伴うことから、最終焼結体のN量を0.002%未満とすることは困難である。従ってN量は0.002~0.04%とすることが好ましい。

**【0019】**本発明のR-Fe-B系焼結型永久磁石においては、Feの一部をNb, Al, Co, Ga, Cuのうち1種類又は2種類以上で置換することができ以下に各元素の置換量(ここでは置換後の永久磁石の全組成に対する重量百分率)の限定の理由を説明する。Nbの置換量は0.1~2.0%とされる。Nbの添加によって、焼結過程でNbのほう化物が生成し、これが結晶粒の異常粒成長を抑制する。Nbの置換量が0.1%より少ないと結晶粒の異常粒成長の抑制効果が十分ではなくなる。一方、Nbの置換量が2.0%を越えると、Nbのほう化物の生成量が多くなるため残留磁束密度Brが低下する。Alの置換量は0.02~2.0%とされる。Alの添加は保磁力iHcを高める効果がある。Alの置換量が0.02%より少ないと保磁力の向上効果が少ないと置換量が2.0%を越えると、残留磁束密度Brが急激に低下する。Coの置換量は0.3~5.0%とされる。Coの添加はキューリ点の向上即ち飽和磁化の温度係数の改善をもたらす。Coの置換量が0.3%より少ないと場合には、温度係数の改善効果は小さい。Coの置換量が5.0%を越えると、残留磁束密度Br、保磁力iHcが共に急激に低下する。Gaの置換量は0.01~0.5%とされる。Gaの微量添加は保磁力iHcの向上をもたらすが、置換量が0.0

1%より少ないと場合には、添加効果は小さい。一方、Gaの置換量が0.5%を越えると、残留磁束密度Brの低下が顕著になるとともに保磁力iHcも低下する。Cuの置換量は0.01~1.0%とされる。Cuの微量添加は保磁力iHcの向上をもたらすが、置換量が1.0%を越えるとその添加効果は飽和する。添加量が0.01%より少ないと場合には、保磁力iHcの向上効果は小さい。

#### 【0020】

**【発明の実施の態様】**以下、本発明を実施例をもって具体的に説明するが、本発明の内容はこれに限定されるものではない。

(実施例1) 重量百分率でNd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, Al 0.10%, O 0.03%, Co 0.005%, N 0.004%, 残部Feの組成を有する、厚さが0.2~0.5mmの薄帯状合金を、ストリップキャスト法で作製した。この薄帯状の合金を、Arガス雰囲気中で1000°Cで2時間加熱した。次に水素炉を使用し、この薄帯状の合金を常温で水素ガス雰囲気中で水素吸収させ、自然崩壊させた。次いで炉内を真空排気しつつ550°Cまで薄帯状の合金を加熱し、その温度で1時間保持して脱水素処理を行った。崩壊した合金を窒素ガス雰囲気中で機械的に破碎して、32mesh以下の原料粗粉とした。この原料粗粉の組成を分析したところ、Nd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, Al 0.10%, O 0.14%, C 0.02%, N 0.007%, 残部Feという分析値を得た。この原料粗粉50kgをジェットミル内に装入した後、ジェットミル内部をN2ガスで置換し、N2ガス中の酸素濃度を酸素分析計値で0.100vol%とした。次いで、粉碎圧力7.0kg/cm2、原料粗粉の供給量10kg/Hrの条件で粉碎した。微粉の平均粒度は4.3μmであった。この微粉を、金型キャビティ内で12kOeの配向磁界を印加しながら0.8ton/cm2の成形圧で成形した。配向磁界の印加方向は、成形方向と垂直である。成形体は、4.0×10-4torrの条件下で15°C/分の昇温速度で1100°Cまで昇温し、その温度で2時間保持して焼結した。焼結体の組成を分析したところ、Nd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, Al 0.10%, O 0.55%, C 0.07%, N 0.012%, 残部Feという分析値を得た。この焼結体の、磁石主相結晶の総面積に対する、結晶粒径が10μm以下の主相結晶粒の面積の和は94%、結晶粒径が13μm以上の主相結晶粒の面積の和は3%であった。この焼結体にArガス雰囲気中で900°C×2時間と550°C×1時間の熱処理を各1回施した。機械加工後磁気特性を測定したところ、表2に示すような良好な値を得た。この永久磁石の耐蝕性を評価するために、磁石を10mm×10mm×2mmの一定寸法に加工後、その表面に10μmのNiメッキを施した。次いでこの試料を2気圧、120°C、湿度100%の条件に放置し、時間の経過に対するNiメッキのハクリ程度を調べた。表2に示すように、2000時間を経過してもNiメッキに異常が認められず、良好な耐蝕性を示した。

**【0021】**(実施例2) 重量百分率でNd 19.5%, Pr 6.5

%, Dy 5.5%, B 1.0%, Nb 0.5%, Al 0.2%, Co 2.0%, Ga 0.1%, O 0.02%, C 0.005%, N 0.003%, 残部Feの組成を有する、厚さが0.2~0.4mmの薄帯状合金を、ストリップキャスト法で作製した。この薄帯状の合金を、Arガス雰囲気中で1100°Cで1時間加熱した。次に水素炉を使用し、この薄帯状の合金を常温で水素ガス雰囲気中で水素吸収させ、自然崩壊させた。次いで炉内を真空排気しつつ550°Cまで薄帯状の合金を加熱し、その温度で1時間保持して脱水素処理を行った。崩壊した合金を窒素ガス雰囲気中で機械的に破碎して、32mesh以下の原料粗粉とした。この原料粗粉の組成を分析したところ、Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, Al 0.2%, Co 2.0%, Ga 0.10%, O 0.12%, C 0.02%, N 0.007%, 残部Feという分析値を得た。この原料粗粉50kgをジェットミル内に装入した後、ジェットミル内部をN<sub>2</sub>ガスで置換し、N<sub>2</sub>ガス中の酸素濃度を酸素分析計値で0.15%とした。次いで、粉碎圧力8.0kg/cm<sup>2</sup>、原料粗粉の供給量12kg/Hrの条件で粉碎した。微粉の平均粒度は4.6 μmであった。この微粉を、金型キャビティ内で8kOeの配向磁界を印加しながら1.5ton/cm<sup>2</sup>の成形圧で成形した。配向磁界の印加方向は、成形方向と垂直である。成形体は、5.0×10-4torrの条件下で15°C/分の昇温速度で1080°Cまで昇温し、その温度で3時間保持して焼結した。焼結体の組成を分析したところ、Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, Al 0.2%, Co 2.0%, Ga 0.10%, O 0.48%, C 0.06%, N 0.008%, 残部Feという分析値を得た。この焼結体の、磁石主相結晶の総面積に対する、結晶粒径が10 μm以下の主相結晶粒の面積の和は90%、結晶粒径が13 μm以上の主相結晶粒の面積の和は6%であった。この焼結体にArガス雰囲気中で900°C×2時間と600°C×1時間の熱処理を各1回施した。機械加工後磁気特性を測定したところ、表2に示すような良好な値を得た。この永久磁石の耐蝕性を評価するために、磁石を10mm×10mm×2mmの一定寸法に加工後、その表面に10 μmのNiメッキを施した。次いでこの試料を2気圧、120°C、湿度100%の条件に放置し、時間の経過に対するNiメッキのハクリ程度を調べた。表2に示すように、2000時間を経過してもNiメッキに異常が認められず、良好な耐蝕性を示した。また、得られた永久磁石の金属組織写真を図4に示す。図5の金属組織写真に比し、組織が微細かつ均一であることがわかる。

【0022】(実施例3)重量百分率でNd 25.8%, Pr 5.5%, Dy 1.2%, B 1.05%, Al 0.08%, Co 2.0%, Ga 0.09%, Cu 0.1%, O 0.03%, C 0.005%, N 0.005%, 残部Feの組成を有する、厚さが0.1~0.5mmの薄帯状合金を、ストリップキャスト法で作製した。この薄帯状の合金を、Arガス雰囲気中で900°Cで2時間加熱した。次に水素炉を使用し、この薄帯状の合金を常温で水素ガス雰囲気中で水素吸収させ、自然崩壊させた。次いで炉内を真空排気しつつ550°Cまで薄帯状の合金を加熱し、その温度で1時間保

持して脱水素処理を行った。崩壊した合金を窒素ガス雰囲気中で機械的に破碎して、32mesh以下の原料粗粉とした。この原料粗粉の組成を分析したところ、Nd 25.8%, Pr 5.5%, Dy 1.2%, B 1.05%, Al 0.08%, Ga 0.09%, Cu 0.1%, O 0.14%, C 0.03%, N 0.009%, 残部Feという分析値を得た。この原料粗粉50kgをジェットミル内に装入した後、ジェットミル内部をArガスで置換し、Arガス中の酸素濃度を酸素分析計値で0.050vol%とした。次いで、粉碎圧力7.5kg/cm<sup>2</sup>、原料粗粉の供給量9kg/Hrの条件で粉碎した。微粉の平均粒度は4.7 μmであった。この原料スラリーを、金型キャビティ内で8kOeの配向磁界を印加しながら0.6ton/cm<sup>2</sup>の成形圧で湿式成形した。配向磁界の印加方向は、成形方向と垂直である。成形体は、4.0×10-4torrの条件下で15°C/分の昇温速度で1100°Cまで昇温し、その温度で2時間保持して焼結した。焼結体の組成を分析したところ、Nd 25.8%, Pr 5.5%, Dy 1.2%, B 1.05%, Al 0.08%, Ga 0.09%, Cu 0.1%, O 0.35%, C 0.07%, N 0.025%, 残部Feという分析値を得た。この焼結体の、磁石主相結晶の総面積に対する、結晶粒径が10 μm以下の主相結晶粒の面積の和は88%、結晶粒径が13 μm以上の主相結晶粒の面積の和は7%であった。この焼結体にArガス雰囲気中で900°C×2時間と580°C×1時間の熱処理を各1回施した。機械加工後磁気特性を測定したところ、表2に示すような良好な値を得た。この永久磁石の耐蝕性を評価するために、磁石を10mm×10mm×2mmの一定寸法に加工後、その表面に10 μmのNiメッキを施した。次いでこの試料を2気圧、120°C、湿度100%の条件に放置し、時間の経過に対するNiメッキのハクリ程度を調べた。表2に示すように、2000時間を経過してもNiメッキに異常が認められず、良好な耐蝕性を示した。

【0023】(比較例1)実施例1で作製した薄帯状の合金を、熱処理をおこなわずに直接水素炉に入れ、常温で水素ガス雰囲気中で水素吸収させ、自然崩壊させた。その後、実施例1と同じ条件で脱水素処理と機械的破碎をおこない、32mesh以下の原料粗粉とした。この原料粗粉の組成を分析したところ、重量百分率でNd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, Al 0.10%, O 0.11%, C 0.02%, N 0.006%, 残部Feという分析値を得た。この原料粗粉を、実施例1と同一の条件で微粉碎した。得られた微粉の平均粒度は4.6 μmと、実施例1の場合に比べて粗かった。成形、焼結、熱処理、耐蝕性の評価などの以降の工程も、実施例1と同一の条件で行った。焼結体の組成を分析したところ、Nd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, Al 0.10%, O 0.51%, C 0.06%, N 0.015%, 残部Feという分析値を得た。この焼結体の、磁石主相結晶の総面積に対する、結晶粒径が10 μm以下の主相結晶粒の面積の和は77%、結晶粒径が13 μm以上の主相結晶粒の面積の和は14%であった。この永久磁石の磁気特性を評価したところ、表2に示すように、実施例1の値に比べ

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てBr, iHc共若干低い値であった。また、この永久磁石の耐蝕性は、表2に示すように1000時間を経過してもNiメッキに異常が認められず実用上全く問題ない水準にあることがわかったが、1500時間の経過でNiメッキのわずかなハクリが発生し、実施例1で製造した焼結体との比較では耐蝕性に劣ることが判明した。

【0024】(比較例2)実施例2と同一の組成を有するR-Fe-B系合金インゴットを作製した。この合金の組成分析値は重量百分比率でNd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, Al 0.2%, Co 2.0%, Ga 0.1%, O 0.01%, C 0.004%, N 0.002%, 残部Feであった。合金の組織中に $\alpha$ -Feの析出が認められたため、これを消去するため、合金インゴットにアルゴンガス雰囲気中で1100°C × 6時間の液体化処理を施した。次に合金インゴットを水素炉中に入れ、常温で水素吸蔵させて自然崩壊させた。自然崩壊後の合金を、実施例2と同一の条件で脱水素處理と機械的破碎し、32mesh以下の原料粗粉とした。この原料粗粉の組成を分析したところ、重量百分率でNd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, Al 0.2%, Co 2.0%, Ga 0.1%, O 0.09%, C 0.02%, N 0.006%, 残部Fe

という分析値を得た。この原料粗粉を、実施例2と同一\*

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\*の条件で微粉碎した。得られた微粉の平均粒度は5.1 $\mu$ mと、実施例1の場合に比べて粗かった。成形、焼結、熱処理、耐蝕性の評価などの以降の工程も、実施例2と同一の条件でおこなった。焼結体の組成を分析したところ、Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, Al 0.2%, Co 2.0%, Ga 0.1%, O 0.09%, C 0.02%, N 0.006%, 残部Feという分析値を得た。この焼結体の、磁石主相結晶の総面積に対する、結晶粒径が10 $\mu$ m以下の主相結晶粒の面積の和は65%、結晶粒径が13 $\mu$ m以上の主相結晶粒の面積の和は19%であった。金属組織写真を図5に示す。この永久磁石の磁気特性を評価したところ、表2に示すように、実施例2の値とほぼ同等の良好な値であった。また、この永久磁石の耐蝕性は、表2に示すように700時間を経過してもNiメッキに異常が認められず実用上全く問題ない水準にあることがわかったが、1000時間の経過でNiメッキの一部にわずかなハクリが発生し、実施例2で製造した永久磁石との比較では耐蝕性に劣ることが判明した。

10 【0025】

20 【表2】

|      | 焼結体分析値(wt%) |      |      |       | 磁気特性   |          |                            | 主相結晶粒の総面積に対する特定寸法の主相結晶粒の面積の和の割合(%)<br>当10 $\mu$ m<br>当13 $\mu$ m | 耐蝕性の評価結果 |  |
|------|-------------|------|------|-------|--------|----------|----------------------------|--|----------|--|
|      | Nd+Pr+Dy    | O    | C    | N     | Br(kG) | iHc(kOe) | (BH) <sub>max</sub> (MGoe) |  |          |  |
| 実施例1 | 32.0        | 0.55 | 0.07 | 0.012 | 13.1   | 16.0     | 41.2                       | 94   | 3        | 2000Hr 経過でNiメッキに異常なし                                 |
| 〃2   | 31.5        | 0.48 | 0.06 | 0.008 | 12.8   | 24.6     | 39.4                       | 90   | 6        | 2000Hr 〃   |
| 〃3   | 32.5        | 0.35 | 0.07 | 0.025 | 13.1   | 15.5     | 40.9                       | 88   | 7        | 2000Hr 〃   |
| 比較例1 | 32.0        | 0.51 | 0.08 | 0.015 | 12.9   | 15.4     | 39.7                       | 77   | 14       | 1000Hr 経過でNiメッキに異常なし<br>1500Hr 経過でNiメッキにわずかなハクリが発生   |
| 〃2   | 31.5        | 0.42 | 0.06 | 0.007 | 12.8   | 23.7     | 39.2                       | 65   | 19       | 700Hr 経過でNiメッキに異常なし<br>1000Hr 経過でNiメッキの一部にわずかなハクリが発生 |

【発明の効果】本発明により、磁気特性を低下させずに、優れた耐食性を有するR-Fe-B系焼結型永久磁石が得られる。

#### 【図面の簡単な説明】

【図1】磁石主相結晶の総面積に対する結晶粒径が10 $\mu$ m以下の主相結晶粒の面積の和の割合と、磁石主相結晶の総面積に対する結晶粒径が13 $\mu$ m以上の主相の結晶

粒の面積の和の割合と、耐蝕性の加速試験での、Niメッキのハクリ開始が生じるまでの経過時間との関係を示した図である。

【図2】ストリップキャスト法で作製した薄帯状合金の断面の金属組織写真である。

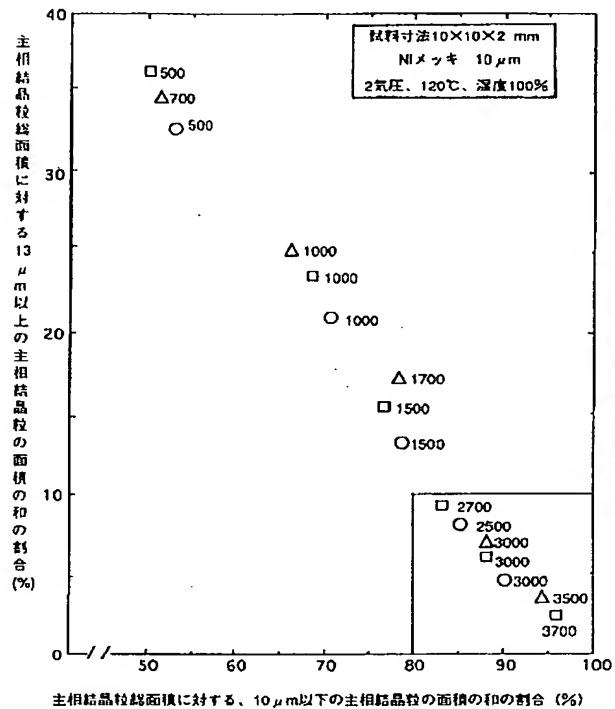
【図3】ストリップキャスト法で作製した薄帯状合金を1000°Cで熱処理した後の断面の金属組織写真であ

13

る。

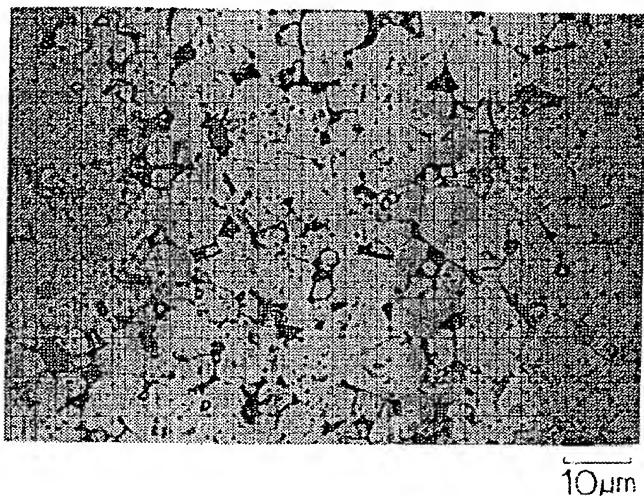
【図4】 磁石主相の総面積に対する結晶粒径が $10\mu\text{m}$ 以下の主相結晶粒の面積の和が90%、結晶粒径が $13\mu\text{m}$ 以上の主相結晶粒の面積の和が6%である焼結型永久磁石の金属組織写真である。

【図1】



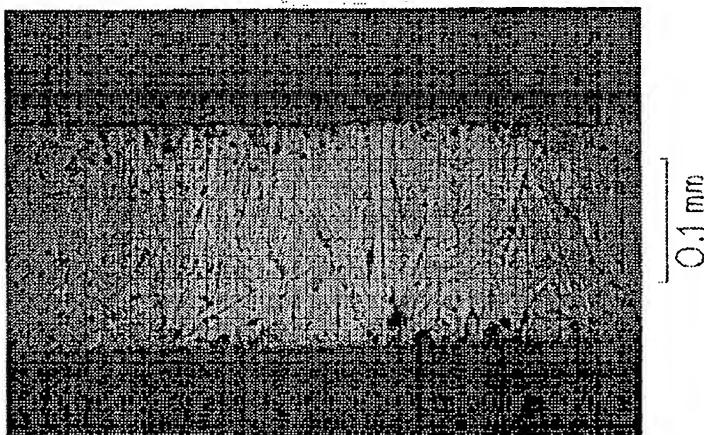
【図4】

図面代用写真



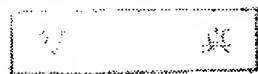
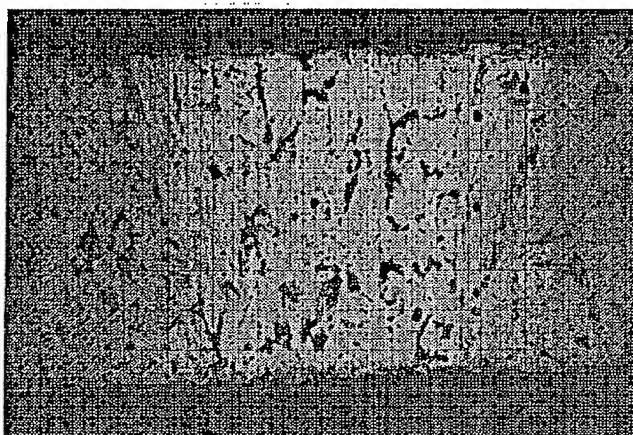
【図2】

図面代用写真



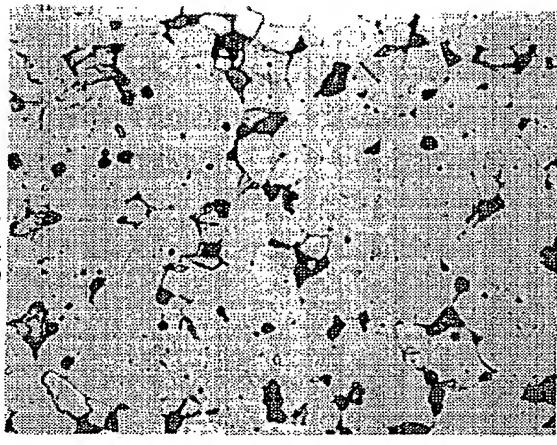
【図3】

顕微鏡写真



【図5】

顕微鏡写真



10μm

# PATENT ABSTRACTS OF JAPAN

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(22)Date of filing : 17.04.1996 (72)Inventor : UCHIDA KIMIO  
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## (54) SINTERED PERMANENT MAGNET

### (57)Abstract:

PROBLEM TO BE SOLVED: To improve corrosion resistance by making the main phase crystal particle diameters of a magnet to be not more than a specified value in the R-Fe-B system sintered permanent magnet with rare earth and oxygen of the specified range amounts.

SOLUTION: In the sintered permanent magnet, composition where R (R is one type or more than two types of rare earth elements containing Y) is 28.0-33.0%, B is 0.5-2.0%, O is 0.3-0.7% and a remaining part is Fe at a weight percentage is provided, and the sum of the areas of main phase crystal particles whose crystal

particle diameters are not more than 10 $\mu$ m is not more than 10% against the total area of the magnetic main phase. In the sintered permanent magnet, a part of Fe is substituted for one type or more than two types among Nb 0.1-2.0%, Al 0.02-2.0%, Co 0.3-5.0%, Ga 0.01-0.5% and Cu 0.01-1.0 or the value of coercive force iHc is made to be not less than 13.0kOe. Thus, the R-Fe-B system sintered permanent magnet having superior corrosion resistance can be obtained without deteriorating a magnetic characteristic.

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## **CLAIMS**

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**[Claim(s)]**

**[Claim 1]** It has the presentation of Remainder Fe with weight percent R(one-sort [ in the rare earth elements in which R contains Y ], or two sorts or more)28.0-33.0%, B 0.5-2.0%, and O 0.3-0.7%. The sintering mold permanent magnet with which the diameter of crystal grain is characterized by 80% or more and crystal grain being [ the sum of the area of the main phase crystal grain 13 micrometers or more ] 10% or less for the sum of the area of the main phase crystal grain 10 micrometers or less to the gross area of the magnet main phase crystal grain.

**[Claim 2]** The sintering mold permanent magnet according to claim 1 which permutes a part of Fe by one sort or two sorts or more in 0.1 - 2.0% of Nb(s), 0.02 - 2.0% of aluminum, 0.3 - 5.0% of Co(es), 0.01 - 0.5% of Ga(s), and 0.01 - 1.0% of Cu(s).

**[Claim 3]** The sintering mold permanent magnet according to claim 1 or 2 whose value of coercive force iHc is 13.0 or more kOes.

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**[Translation done.]**

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the engine-performance improvement of the rare earth magnet of a R-Fe-B system.

[0002]

[Description of the Prior Art] A R-Fe-B system (one-sort [ in the rare earth elements in which R contains Y ], or two sorts or more) sintering mold permanent magnet attracts attention as an aperiodic compass in a sintering mold rare earth permanent magnet, and it is used in the large field. This R-Fe-B system sintering mold permanent magnet has fundamentally the structure which consists of the three phase circuit of R<sub>2</sub>Fe<sub>14</sub>B phase (the main phase), a RFe<sub>7</sub>B<sub>6</sub> phase (Brich phase), and R<sub>85</sub>Fe<sub>15</sub> phase (Rrich phase). It is \*\*\*\* in presentation at rare earth elements -- it originates in existence of a Rrich phase and such three-phase-circuit structure, and compared with a Sm-Co system sintering mold permanent magnet, corrosion resistance is inferior, and a R-Fe-B system sintering mold permanent magnet is one of the faults until it results [ from the time of development of this permanent magnet ] in current. Although there is no established theory about the mechanism of the corrosion of a R-Fe-B system sintering mold permanent magnet, since the gestalt of the corrosion on the basis of a Rrich phase is common, there is also a view with the anode plate corrosion which made the Rrich phase the anode plate. Surely, by decreasing the amount of the rare earth elements of a R-Fe-B system sintering mold permanent magnet, the amount of the Rrich phase inside the sintered compact decreases, and the

gestalt of a phase is made detailed, and the corrosion resistance of a permanent magnet improves corresponding to this. Therefore, it is the one approach of a corrosion-resistant improvement of a R-Fe-B system sintering mold permanent magnet to decrease the amount of rare earth elements.

[0003] As for the rare earth permanent magnet of the sintering mold containing a R-Fe-B system, it is common to be manufactured according to the powder metallurgy-process of dissolving a raw material metal, grinding, fabricating and sintering it, heat-treating it and processing into mold the ingot obtained by carrying out teeming. However, since it contains rare earth elements so much, chemically, the alloy powder which grinds an ingot and is obtained is very activity, it oxidizes in atmospheric air and the amount of content oxygen increases it. By this, with the sintered compact after sintering, some rare earth elements form an oxide and effective rare earth elements decrease magnetically. For this reason, in order to realize the level of practical magnetic properties, for example,  $iH_c >= 13kOe$ , it is necessary to increase the amount of the rare earth elements of a R-Fe-B system sintering mold permanent magnet, and the addition of the rare earth elements which exceed 31% at the rate of percent by weight is adopted at the charge of real material. For this reason, the corrosion resistance of an old R-Fe-B system sintering mold permanent magnet was not enough.

[0004]

[Problem(s) to be Solved by the Invention] This invention tends to improve sharply the corrosion resistance of the R-Fe-B system sintering mold permanent magnet described above.

[0005]

[Means for Solving the Problem] In order to improve the corrosion resistance of a R-Fe-B system sintering mold permanent magnet, as a result of examining many things, in the R-Fe-B system sintering mold permanent magnet of the amount of rare earth of the amount of specific range, and the amount of oxygen, by making the diameter of the magnet main phase crystal grain below into a specific value, this invention persons find out that corrosion resistance improves, and result in

this invention.

[0006] Hereafter, this invention is explained concretely. The sintering mold permanent magnet in this invention has the presentation of Remainder Fe with weight percent R(one-sort [ in the rare earth elements in which R contains Y ], or two sorts or more)28.0-33.0%, B 0.5-2.0%, and O 0.3-0.7%. The sum of the area of the main phase crystal grain 10 micrometers or less is characterized by the diameter of crystal grain being [ the sum of the area of the main phase crystal grain 13 micrometers or more ] 10% or less 80% or more to the gross area of the magnet main phase by the diameter of crystal grain. Moreover, in this invention sintering mold permanent magnet, a part of Fe can be permuted by one sort or two sorts or more in 0.1 - 2.0% of Nb(s), 0.02 - 2.0% of aluminum, 0.3 - 5.0% of Co(es), 0.01 - 0.5% of Ga(s), and 0.01 - 1.0% of Cu(s).

[0007] this invention persons found out that the especially excellent corrosion resistance was discovered by the diameter dependency of crystal grain being in the corrosion resistance of the R-Fe-B system sintering mold permanent magnet which has the above-mentioned presentation, and making the diameter of the magnet main phase crystal grain below into a specific value. There might be various approaches in a definition and measurement of the diameter of magnet crystal grain, and although it was not the most important, the particle size to the gross area of the magnet main phase made artificers the scale which the particle size to the gross area of the magnet main phase of the sum of the area of the main phase crystal grain below a fixed dimension shows the condition of the diameter of magnet crystal grain the sum of the area of the main phase crystal grain more than a fixed dimension be comparatively alike comparatively the same. Suppose that the effectiveness of this invention is explained using this scale below. Moreover, the measurement which hits computing this rate gazed at the crystalline structure of the target R-Fe-B system sintering mold permanent magnet under the microscope made from OLYMPUS (trade name VANOX), and was performed by feeding this image into the image processing system made from NIRECO (trade name LUZEX2) directly.

[0008] this invention persons performed the following evaluations about the diameter of the main phase crystal grain of a R-Fe-B system sintering mold permanent magnet which has the presentation shown in a claim, and corrosion-resistant relation, and obtained the result as shown in drawing 1 . Drawing 1 shows the relation of a between [ transient ] until HAKURI initiation of nickel plating [ the diameter of crystal grain to the gross area of the magnet main phase crystal ] of the diameter [ as opposed to the gross area of the magnet main phase crystal comparatively the same ] of crystal grain of the sum of the area of the main phase crystal grain 10 micrometers or less by the accelerated test of comparatively corrosion-resistant of the sum of the area of crystal grain with a main phase of 13 micrometers or more arises. O The sintered compact with which the mark has the presentation of Nd 22.8%, Pr 6.7%, Dy 2.0%, B 1.0%, aluminum 1.0%, O 0.45%, C 0.08%, N 0.015%, and Remainder Fe at the rate of percent by weight, \*\* The sintered compact with which the mark has the presentation of Nd 31.0%, Dy 1.0%, B 1.05%, aluminum 0.05%, Co 2.0%, Ga 0.09%, O 0.55%, C 0.07%, N 0.008%, and Remainder Fe at the rate of percent by weight, \*\* mark shows Nb 1.0%, aluminum 0.2%, Co 2.0%, Cu 0.08%, O 0.35%, C 0.06%, N 0.030%, and the sintered compact that has the presentation of Remainder Fe at the rate of percent by weight Nd 23.0%, Pr 5.0%, Dy 4.5%, and B1.1%. In the accelerated test in this case, 15-micrometer nickel plating was performed to that front face after processing a magnet into a 10mmx10mmx2mm dimension, and, subsequently to the conditions of two atmospheric pressures, 120 degrees C, and 100% of humidity, the sample was left. Drawing 1 shows that the diameter of crystal grain becomes the thing excellent in especially the corrosion resistance of the R-Fe-B system sintering mold permanent magnet which has the presentation shown in a claim when the sum of the area of the main phase crystal grain 10 micrometers or less is 80% or more and the diameter of crystal grain is [ the sum of the area of the main phase crystal grain 13 micrometers or more ] 10% or less to the gross area of the crystal of the magnet main phase. Therefore, the magnitude of the magnet main phase crystal

grain is specified above.

[0009] If this cause is presumed, in the permanent magnet sintered compact with which the comparatively big main phase crystal grain exists, the volume of the opening section which grain boundary 3 importance is specifically that seed slack part, and is filled up with this Ndrich phase although the opening section between the main phase crystal grain and the Ndrich phase which is very easy to oxidize here exist will become large relatively. Although it is moisture in the factor which brings about corrosion destruction, for example, this accelerated test, the permeability of such a factor is good and is considered that the condition of being easy to happen in chain reaction has destruction of the grain boundary. The above explains that the diameter dependency of the main phase crystal grain is in the corrosion resistance of the R-Fe-B system sintering mold permanent magnet which has the presentation shown in a claim by showing an example of research results, such as this invention person.

[0010] Although the approach of controlling the diameter of crystal grain of the main phase of a R-Fe-B system sintering mold permanent magnet which has the presentation of a claim to the thing of the above-mentioned convention range is not necessarily the most important and the combination of various approaches or those approaches can attain, by research of artificers, it is accompanied by remarkable difficulty by the usual approach. The approach of carrying out pulverization of the raw material coarse powder by pulverizing, and carrying out metal mold shaping of these fines in a field in manufacture of a R-Fe-B system sintering mold permanent magnet, generally, and acquiring a Plastic solid, sintering this and using as a sintered compact is taken. For example, when performing pulverizing using a jet mill, fines with a predetermined average grain size and particle size distribution can be obtained by controlling the pressure of the gas at the time of grinding, the speed of supply of coarse powder, etc. Moreover, the particle size distribution of fines are also controllable by performing a classification if needed. Thus, in fabricating the produced fines and sintering, it is not necessarily impossible by choosing still more suitable sintering

temperature, time amount, and pattern to make the diameter of crystal grain of the main phase of a R-Fe-B system sintering mold permanent magnet into the thing of the above-mentioned convention range. However, many conditions needed to be set up, this needed to be controlled and it turned out that it is very difficult to manufacture the sintered compact which has a predetermined diameter of crystal grain with sufficient repeatability.

[0011] This invention persons are easy to make into the above-mentioned convention range the diameter of the main phase of a R-Fe-B system sintering mold permanent magnet of crystal grain which has the presentation of a claim, as a result of searching for the approach for which it is suitable on mass production, heat-treated the R-Fe-B system quenching thin band-like alloy which has the predetermined presentation manufactured by the approach called the so-called strip cast method in a predetermined temperature requirement, and found out the approach of grinding this and using as raw material coarse powder. Moreover, in grinding the thin band-like alloy after heat treatment, it is effective when carrying out after performing post-dehydrogenation treatment which carried out spontaneous disintegration by hydrogen absorption raises the pulverizing engine performance. Drawing 2 is a cross-section organization of the thin band-like alloy manufactured by the strip cast method which has the presentation of N 0.004%, C 0.007%, and Remainder Fe at the rate of percent by weight Nd 22.7%, Pr 7.6%, Dy 1.5%, B 1.05%, aluminum 0.05%, and O0.01% (as cast). The detailed dendrite-like organization exists. The phase which the phase observed by white in a photograph has few amounts of rare earth, and is equivalent to the main phase of a permanent magnet sintered compact, and the phase observed black are phases equivalent to the Rrich phase of a permanent magnet sintered compact with many amounts of rare earth. When the band-like alloy currently distributed minutely is used as this Rrich phase shows drawing 2 since this Rrich phase serves as an origin of destruction at the time of pulverizing, it is easy to generate fines fine particle size and uniform probable. Therefore, manufacture of the sintered compact which, comparatively easy moreover, has the particle size

distribution of a claim with sufficient repeatability is attained, without managing strictly many conditions at the time of pulverizing and sintering. However, even if it grinds this thin band-like alloy (with quenching casting) directly as it is, it considers as raw material coarse powder and it pulverizes this, the particle size distribution of good fines are not acquired and the diameter of the main phase crystal grain concerning this invention is not obtained in the sintered compact which fabricated and sintered this. This reason is because the front face of a thin band-like alloy hardens and the grindability-ed at the time of pulverizing is remarkably worsened by quenching casting.

[0012] this invention persons found out that it was effective to heat-treat this thin band-like alloy in a specific temperature requirement, and to remove hardening of a thin band-like alloy front face as a means to solve this problem. Temperature of heat treatment is made into 800 degrees C - 1100 degrees C. This is because removal of hardening of heat treatment temperature at less than 800 degrees C is inadequate. Moreover, it is because a reaction arises between thin band-like alloys at the time of heat treatment and difficulty arises in processing at a back process at temperature higher than 1100 degrees C. Since it is the thin band-like alloy which contains activity rare earth elements so much, it cannot be overemphasized that it is necessary to perform heat treatment in an inert gas ambient atmosphere or a substantial vacuum. Moreover, after carrying out occlusion of the hydrogen to the thin band-like alloy after heat treatment, carrying out spontaneous disintegration as mentioned above and performing dehydrogenation treatment, it is still more effective to coarse-powder-ize this, when raising pulverizing nature. In addition to the removal effectiveness of hardening of the thin band-like alloy front face by heat treatment, this is because the embrittlement effectiveness of a Rrich phase joins the Lord inside the thin band-like alloy by hydrogen.

[0013] A thin band-like alloy is heat-treated or (1Hr) ground on various conditions, and it considers as coarse powder, and this is pulverized on the same conditions and the condition of the diameter of the main phase crystal grain of the sintered

compact at the time of fabricating and sintering is shown in Table 1.

[0014]

[Table 1]

| 評価項目   |                                   | 薄体状合金熱処理<br>温度(℃)     | 急冷鋳造<br>まま | 700  | 800  | 900  | 1000 | 1100 | 1200 |
|--------|-----------------------------------|-----------------------|------------|------|------|------|------|------|------|
| 水素吸蔵なし | 主相結晶粒総面積に対する特定寸法の主相結晶粒の面積の和の割合(%) | 10μ以下                 | 67         | 75   | 84   | 88   | 88   | 90   | 90   |
|        |                                   | 13μ以上                 | 25         | 18   | 8    | 6    | 6    | 5    | 5    |
|        | 磁気特性                              | Br (KG)               | 12.8       | 12.8 | 13.1 | 13.1 | 13.2 | 13.2 | 13.2 |
|        |                                   | I <sub>Hc</sub> (kOe) | 15.2       | 15.2 | 16.0 | 15.9 | 15.8 | 15.8 | 15.8 |
| 水素吸蔵あり | 主相結晶粒総面積に対する特定寸法の主相結晶粒の面積の和の割合(%) | 10μ以下(%)              | 73         | 77   | 86   | 90   | 94   | 95   | 95   |
|        |                                   | 13μ以上(%)              | 18         | 13   | 6    | 4    | 3    | 3    | 2    |
|        | 磁気特性                              | Br (KG)               | 12.9       | 12.9 | 13.1 | 13.1 | 13.2 | 13.2 | 13.2 |
|        |                                   | I <sub>Hc</sub> (kOe) | 15.5       | 15.5 | 16.1 | 16.1 | 16.0 | 16.0 | 16.0 |

[0015] By heat-treating a thin band-like alloy at the temperature of 800 degrees C or more, and using this from Table 1, shows that the sintered compact which has the rate of the main phase particle size shown in a claim is obtained. Moreover, as mentioned above, the effectiveness of hydrogen processing is also in \*\*. The condition of the main phase particle size in heat treatment at 700 degrees C is almost equivalent to a thing [ with quenching casting carried out ] from Table 1 to coincidence. In the heat treatment temperature of 700 degrees C, it turns out that it is inadequate for removal of the hard facing of a thin band alloy. Especially this invention persons found out to coincidence that heat treatment at the temperature of 800 degrees C or more of a thin band-like alloy brought about the improvement effectiveness of Br among magnetic properties. Similarly a result is shown in Table 1. Although Br of the permanent magnet sintered compact by the thin band-like alloy of a quenching casting condition and 700-degree C heat

treatment is 12.8 - 12.9KG, when the thin band-like alloy of 800 degrees C and 900-degree C heat treatment is used, Br increases from Table 1 rapidly with 13.1KG. Heat treatment temperature increases in slightly Br obtained as a result at 1000 degrees C, and it is set to 13.2KG. In the heat treatment temperature of 1100 degrees C and 1200 degrees C, the increment in Br reaches saturation and is not different from 13.2KG. The metal texture photograph of the thin object-like alloy which heat-treated the metal texture photograph of the thin object-like alloy after quenching casting at 1000 degrees C after quenching casting to drawing 2 among the thin object-like alloys shown in Table 1 is shown in drawing 3 . any of the black organization which is equivalent to the white organization equivalent to the main phase in a thin object-like alloy, and a Rrich phase with heat treatment when drawing 2 and drawing 3 are compared -- although -- it turns out that it is made big and rough. From these things, since the organization which consists of phases which are equivalent to the main phase and a Rrich phase with a thin object-like alloy with quenching casting is detailed, this invention person etc.

When fines are manufactured using this, many things with a polycrystal condition exist in the inside of fines probable, and I cause the fall of the stacking tendency at the time of carrying out metal mold shaping of the fines in a field, and think that Br fall of a permanent magnet sintered compact is brought about. The heat treatment temperature of 700 degrees C of growth of an organization is inadequate, and it does not result in an improvement of a stacking tendency in it. although it is thought that the probability of generating of the fines of a polycrystal condition falls and Br is improved by this although the internal organization of a thin object-like alloy has made it big and rough according to the rise of heat treatment temperature, as long as it judges from the result of Table 1, it is thought that the effectiveness shows up considerably, shows up and is with the heat treatment temperature of 800 degrees C. According to the further increment in the heat treatment temperature of a thin object-like alloy, although Br of the sintered compact obtained improves, it shows the inclination of saturation with the heat treatment temperature of 1000 degrees C or more. In the phase which

reached the condition that the organization inside a thin object-like alloy made this big and rough to some extent, and the fines of a polycrystal condition hardly generated it probable, even if it raises heat treatment temperature further and promotes big and rough-ization of an organization, I hear that it is not reflected as improvement in Br of the sintered compact obtained, and he can understand it.

[0016] As explained to the detail above, the quenching casting thin band-like alloy of the predetermined presentation by the strip cast method By heat-treating in a specific temperature requirement, or performing and carrying out spontaneous disintegration of the hydrogen absorption processing to this, and grinding and coarse-powder-izing this The grindability at the time of pulverizing is improved, and although the permanent magnet sintered compact manufactured using this becomes what has the diameter of the main phase crystal grain shown in the claim which was extremely excellent in corrosion resistance, it has not only it but high magnetic properties. In addition, it is necessary to perform preferably 800-1100-degree C heat treatment time amount of a thin band-like alloy 30 minutes or more at least 15 minutes or more.

[0017] Below, the reason for limitation of a presentation of the R-Fe-B system sintering mold permanent magnet of this invention is explained. The amount of rare earth elements is made into 28.0 - 33.0% with weight percent. If the amount of rare earth elements exceeds 31.0%, the amount of the Rrich phase inside a sintered compact will increase, and a gestalt will also be made big and rough, and corrosion resistance will worsen. On the other hand, the amount of liquid phase required for the eburnation of a sintered compact is insufficient in the amount of rare earth elements being less than 28.0%, a sintered compact consistency falls, and both a residual magnetic flux density Br and the coercive force iHc fall to coincidence among magnetic properties. Therefore, the amount of rare earth elements is made into 28.0 - 33.0%. Moreover, the sintered compact which has a high sintered compact consistency can be easily obtained by making the amount of rare earth elements into 31.0% or more. The amount of O is made into 0.3 - 0.7% with weight percent. When the amount of O exceeds

0.7%, some rare earth elements form an oxide, effective rare earth elements decrease magnetically, and coercive force  $iH_c$  declines. On the other hand, by oxidation at a pulverizing process, it is difficult to make the amount of O of the last sintered compact into less than 0.3%, and the amount of O is made into 0.3 - 0.7%.

[0018] As for the amount of C, it is desirable to consider as 0.15% or less with weight percent. When there are more amounts of C than 0.15%, some rare earth elements form carbide, effective rare earth elements decrease magnetically, and coercive force  $iH_c$  declines. As for the amount of C, considering as 0.12% or less is more desirable, and considering as 0.10% or less is still more desirable. On the other hand, the level of the amount of C of the ingot produced by the dissolution is a maximum of 0.008%, it is difficult to make the amount of C of the last sintered compact below into this value, and, as for the amount of C of a sintered compact, considering as 0.01 - 0.15% is desirable. As for the amount of N, it is desirable to consider as 0.002 - 0.04% with weight percent. If the amount of N exceeds 0.04%, some rare earth elements will form a nitride, effective rare earth elements will decrease magnetically, and coercive force  $iH_c$  will decline. Moreover, since it is accompanied by some nitriding in process of pulverizing, it is difficult to make the amount of N of the last sintered compact into less than 0.002%. Therefore, as for the amount of N, considering as 0.002 - 0.04% is desirable.

[0019] If take and it is in the R-Fe-B system sintering mold permanent magnet of this invention, a part of Fe can be permuted by one kind or two kinds or more in Nb, aluminum, Co, Ga, and Cu, and the reason of limitation of the amount of permutations of each element (weight percent [ here as opposed to the total presentation of the permanent magnet after a permutation ]) is explained below. The amount of permutations of Nb is made into 0.1 - 2.0%. By addition of Nb, the way ghost of Nb generates in a sintering process, and this controls abnormality grain growth of crystal grain. When there are few amounts of permutations of Nb than 0.1%, the depressor effect of abnormality grain growth of crystal grain

becomes less enough. On the other hand, if the amount of permutations of Nb exceeds 2.0%, since the amount of generation of the way ghost of Nb increases, a residual magnetic flux density Br will fall. The amount of permutations of aluminum is made into 0.02 - 2.0%. Addition of aluminum has the effectiveness which heightens coercive force iHc. When there are few amounts of permutations of aluminum than 0.02%, there is little improvement effectiveness of coercive force. If the amount of permutations exceeds 2.0%, a residual magnetic flux density Br will fall rapidly. The amount of permutations of Co is made into 0.3 - 5.0%. Addition of Co brings about the improvement in a curie point, i.e., an improvement of the temperature coefficient of saturation magnetization. When there are few amounts of permutations of Co than 0.3%, the improvement effect of a temperature coefficient is small. If the amount of permutations of Co exceeds 5.0%, both a residual magnetic flux density Br and the coercive force iHc will decline rapidly. The amount of permutations of Ga is made into 0.01 - 0.5%. Although minute amount addition of Ga brings about improvement in coercive force iHc, the addition effectiveness is small when there are few amounts of permutations than 0.01%. On the other hand, if the amount of permutations of Ga exceeds 0.5%, while the fall of a residual magnetic flux density Br becomes remarkable, coercive force iHc will also decline. The amount of permutations of Cu is made into 0.01 - 1.0%. Although minute amount addition of Cu brings about improvement in coercive force iHc, if the amount of permutations exceeds 1.0%, the addition effectiveness will be saturated. When there are few additions than 0.01%, the improvement effectiveness of coercive force iHc is small.

#### [0020]

[The mode of implementation of invention] Hereafter, although this invention is concretely explained with an example, the contents of this invention are not limited to this.

(Example 1) The thin band-like alloy which has the presentation of Nd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, aluminum 0.10%, O 0.03%, C0.005%, N 0.004%, and Remainder Fe with weight percent and whose thickness is 0.2-0.5mm was

produced by the strip cast method. This thin band-like alloy was heated at 1000 degrees C in Ar gas ambient atmosphere for 2 hours. Next, a hydrogen furnace is used, in ordinary temperature, in the hydrogen gas ambient atmosphere, hydrogen absorption of this thin band-like alloy was carried out, and it carried out spontaneous disintegration. Subsequently, the thin band-like alloy was heated to 550 degrees C, carrying out evacuation of the inside of a furnace, it held at the temperature for 1 hour, and dehydrogenation treatment was performed. The collapsed alloy was mechanically crushed in nitrogen-gas-atmosphere mind, and it considered as the raw material coarse powder of 32 or less meshes. When the presentation of this raw material coarse powder was analyzed, the analysis value of Nd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, aluminum 0.10%, O 0.14%, C 0.02%, N 0.007%, and Remainder Fe was acquired. After inserting in 50kg of this raw material coarse powder in a jet mill, N2 gas permuted the interior of a jet mill, and the oxygen density in N2 gas was made into 0.100vol(s)% with the oxygen analyzer value. Subsequently, it ground on condition that amount-of-supply 10 kg/Hr of 7.0kg/cm<sup>2</sup> of grinding pressure force, and raw material coarse powder. The average grain size of fines was 4.3 micrometers. These fines were fabricated with the moulding pressure of 0.8 ton/cm<sup>2</sup>, impressing the orientation field of 12kOe(s) within a metal mold cavity. The impression direction of an orientation field is perpendicular to the shaping direction. The temperature up of the Plastic solid was carried out to 1100 degrees C with 15-degree-C programming rate for /under the conditions of 4.0x10-4torr, and at the temperature, it was held for 2 hours and sintered. When the presentation of a sintered compact was analyzed, the analysis value of Nd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, aluminum 0.10%, O 0.55%, C 0.07%, N 0.012%, and Remainder Fe was acquired. As for the sum of the area of the main phase crystal grain 10 micrometers or less, the diameter of crystal grain to the gross area of the magnet main phase crystal of this sintered compact was [ the diameter of crystal grain of the sum of the area of the main phase crystal grain 13 micrometers or more ] 3% 94%. Heat treatment of 900 degree-Cx 2 hours, and 550 degree-Cx 1 hour was

performed to this sintered compact once each in Ar gas ambient atmosphere. When the magnetic properties after machining were measured, the good value as shown in Table 2 was acquired. In order to evaluate the corrosion resistance of this permanent magnet, the magnet processing-back was performed to the 10mmx10mmx2mm fixed dimension, and 10-micrometer nickel plating was performed to that front face. Subsequently, this sample was left on two atmospheric pressures, 120 degrees C, and the conditions of 100% of humidity, and HAKURI extent of nickel plating to the passage of time was investigated. As shown in Table 2, even if 2000 hours passed, abnormalities were not accepted in nickel plating, but good corrosion resistance was shown.

[0021] (Example 2) The thin band-like alloy which has the presentation of Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, aluminum 0.2%, Co 2.0%, Ga 0.1%, O 0.02%, C 0.005%, N 0.003%, and Remainder Fe with weight percent and whose thickness is 0.2-0.4mm was produced by the strip cast method. This thin band-like alloy was heated at 1100 degrees C in Ar gas ambient atmosphere for 1 hour. Next, a hydrogen furnace is used, in ordinary temperature, in the hydrogen gas ambient atmosphere, hydrogen absorption of this thin band-like alloy was carried out, and it carried out spontaneous disintegration. Subsequently, the thin band-like alloy was heated to 550 degrees C, carrying out evacuation of the inside of a furnace, it held at the temperature for 1 hour, and dehydrogenation treatment was performed. The collapsed alloy was mechanically crushed in nitrogen-gas-atmosphere mind, and it considered as the raw material coarse powder of 32 or less meshes. When the presentation of this raw material coarse powder was analyzed, the analysis value of Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, aluminum 0.2%, Co 2.0%, Ga 0.10%, O 0.12%, C 0.02%, N 0.007%, and Remainder Fe was acquired. After inserting in 50kg of this raw material coarse powder in a jet mill, N2 gas permuted the interior of a jet mill, and the oxygen density in N2 gas was made into 0.15% with the oxygen analyzer value. Subsequently, it ground on condition that amount-of-supply 12 kg/Hr of 8.0kg/cm<sup>2</sup> of grinding pressure force, and raw material coarse

powder. The average grain size of fines was 4.6 micrometers. These fines were fabricated with the moulding pressure of 1.5 ton/cm<sup>2</sup>, impressing the orientation field of 8kOe(s) within a metal mold cavity. The impression direction of an orientation field is perpendicular to the shaping direction. The temperature up of the Plastic solid was carried out to 1080 degrees C with 15-degree-C programming rate for /under the conditions of 5.0x10<sup>-4</sup>torr, and at the temperature, it was held for 3 hours and sintered. When the presentation of a sintered compact was analyzed, the analysis value of Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, aluminum 0.2%, Co 2.0%, Ga 0.10%, O 0.48%, C 0.06%, N 0.008%, and Remainder Fe was acquired. As for the sum of the area of the main phase crystal grain 10 micrometers or less, the diameter of crystal grain to the gross area of the magnet main phase crystal of this sintered compact was [ the diameter of crystal grain of the sum of the area of the main phase crystal grain 13 micrometers or more ] 6% 90%. Heat treatment of 900 degree-Cx 2 hours, and 600 degree-Cx 1 hour was performed to this sintered compact once each in Ar gas ambient atmosphere. When the magnetic properties after machining were measured, the good value as shown in Table 2 was acquired. In order to evaluate the corrosion resistance of this permanent magnet, the magnet processing-back was performed to the 10mmx10mmx2mm fixed dimension, and 10-micrometer nickel plating was performed to that front face. Subsequently, this sample was left on two atmospheric pressures, 120 degrees C, and the conditions of 100% of humidity, and HAKURI extent of nickel plating to the passage of time was investigated. As shown in Table 2, even if 2000 hours passed, abnormalities were not accepted in nickel plating, but good corrosion resistance was shown. Moreover, the metal texture photograph of the obtained permanent magnet is shown in drawing 4 . It compares with the metal texture photograph of drawing 5 , and it turns out that an organization is detailed and uniform.

[0022] (Example 3) The thin band-like alloy which has the presentation of Nd 25.8%, Pr 5.5%, Dy 1.2%, B 1.05%, aluminum 0.08%, Co 2.0%, Ga0.09%, Cu

0.1%, O 0.03%, C 0.005%, N 0.005%, and Remainder Fe with weight percent and whose thickness is 0.1-0.5mm was produced by the strip cast method. This thin band-like alloy was heated at 900 degrees C in Ar gas ambient atmosphere for 2 hours. Next, a hydrogen furnace is used, in ordinary temperature, in the hydrogen gas ambient atmosphere, hydrogen absorption of this thin band-like alloy was carried out, and it carried out spontaneous disintegration. Subsequently, the thin band-like alloy was heated to 550 degrees C, carrying out evacuation of the inside of a furnace, it held at the temperature for 1 hour, and dehydrogenation treatment was performed. The collapsed alloy was mechanically crushed in nitrogen-gas-atmosphere mind, and it considered as the raw material coarse powder of 32 or less meshes. When the presentation of this raw material coarse powder was analyzed, the analysis value of Nd 25.8%, Pr 5.5%, Dy 1.2%, B 1.05%, aluminum 0.08%, Ga 0.09%, Cu 0.1%, O 0.14%, C 0.03%, N 0.009%, and Remainder Fe was acquired. After inserting in 50kg of this raw material coarse powder in a jet mill, Ar gas permuted the interior of a jet mill, and the oxygen density in Ar gas was made into 0.050vol(s)% with the oxygen analyzer value. Subsequently, it ground on condition that amount-of-supply 9 kg/Hr of 7.5kg/cm<sup>2</sup> of grinding pressure force, and raw material coarse powder. The average grain size of fines was 4.7 micrometers. The wet compaction of this raw material slurry was carried out with the moulding pressure of 0.6 ton/cm<sup>2</sup>, impressing the orientation field of 8kOe(s) within a metal mold cavity. The impression direction of an orientation field is perpendicular to the shaping direction. The temperature up of the Plastic solid was carried out to 1100 degrees C with 15-degree-C programming rate for /under the conditions of 4.0x10<sup>-4</sup>torr, and at the temperature, it was held for 2 hours and sintered. When the presentation of a sintered compact was analyzed, the analysis value of Nd 25.8%, Pr 5.5%, Dy 1.2%, B 1.05%, aluminum 0.08%, Ga 0.09%, Cu 0.1%, O 0.35%, C 0.07%, N 0.025%, and Remainder Fe was acquired. As for the sum of the area of the main phase crystal grain 10 micrometers or less, the diameter of crystal grain to the gross area of the magnet main phase crystal of this sintered

compact was [ the diameter of crystal grain of the sum of the area of the main phase crystal grain 13 micrometers or more ] 7% 88%. Heat treatment of 900 degree-Cx 2 hours, and 580 degree-Cx 1 hour was performed to this sintered compact once each in Ar gas ambient atmosphere. When the magnetic properties after machining were measured, the good value as shown in Table 2 was acquired. In order to evaluate the corrosion resistance of this permanent magnet, the magnet processing-back was performed to the 10mmx10mmx2mm fixed dimension, and 10-micrometer nickel plating was performed to that front face. Subsequently, this sample was left on two atmospheric pressures, 120 degrees C, and the conditions of 100% of humidity, and HAKURI extent of nickel plating to the passage of time was investigated. As shown in Table 2, even if 2000 hours passed, abnormalities were not accepted in nickel plating, but good corrosion resistance was shown.

[0023] (Example 1 of a comparison) It puts into a direct hydrogen furnace, without performing heat treatment, and in ordinary temperature, in the hydrogen gas ambient atmosphere, hydrogen absorption of the thin band-like alloy produced in the example 1 was carried out, and it carried out spontaneous disintegration. Then, dehydrogenation treatment and mechanical crushing were performed on the same conditions as an example 1, and it considered as the raw material coarse powder of 32 or less meshes. When the presentation of this raw material coarse powder was analyzed, the analysis value of Nd 23.5%, Pr 7.0%, Dy1.5%, B 1.05%, aluminum 0.10%, O 0.11%, C 0.02%, N 0.006%, and Remainder Fe was acquired with weight percent. This raw material coarse powder was pulverized on the same conditions as an example 1. The average grain size of the obtained fines was coarse compared with 4.6 micrometers and the case of an example 1. The process of henceforth, such as shaping, sintering, heat treatment, and corrosion-resistant evaluation, was also performed on the same conditions as an example 1. When the presentation of a sintered compact was analyzed, the analysis value of Nd 23.5%, Pr 7.0%, Dy 1.5%, B 1.05%, aluminum 0.10%, O 0.51%, C 0.06%, N 0.015%, and Remainder Fe was

acquired. As for the sum of the area of the main phase crystal grain 10 micrometers or less, the diameter of crystal grain to the gross area of the magnet main phase crystal of this sintered compact was [ the diameter of crystal grain of the sum of the area of the main phase crystal grain 13 micrometers or more ] 14% 77%. When the magnetic properties of this permanent magnet were evaluated, as shown in Table 2, compared with the value of an example 1, it was a value with Br and iHc low a little. Moreover, although, as for the corrosion resistance of this permanent magnet, it turned out that abnormalities are not accepted in nickel plating but it is in the level which is practically completely satisfactory even if 1000 hours passed, as shown in Table 2, few breaks away of nickel plating by the 1500 passage of time occurred, and it became clear that it was inferior to corrosion resistance in the comparison with the sintered compact manufactured in the example 1.

[0024] (Example 2 of a comparison) The R-Fe-B system alloy ingot which has the same presentation as an example 2 was produced. The component-analysis values of this alloy were Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, aluminum 0.2%, Co 2.0%, Ga 0.1%, O 0.01%, C 0.004%, N 0.002%, and Remainder Fe at the rate of percent by weight. Since the deposit of alpha-Fe was accepted during the organization of an alloy, in order to eliminate this, liquid-ized processing of 1100 degree-Cx 6 hours was performed to the alloy ingot in the argon gas ambient atmosphere. Next, an alloy ingot is put in all over a hydrogen furnace, in ordinary temperature, hydrogen absorption was carried out and spontaneous disintegration was carried out. Mechanical crushing of the alloy after spontaneous disintegration was carried out with dehydrogenation treatment on the same conditions as an example 2, and it was used as the raw material coarse powder of 32 or less meshes. When the presentation of this raw material coarse powder was analyzed, the analysis value of Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, aluminum 0.2%, Co 2.0%, Ga 0.1%, O 0.09%, C 0.02%, N 0.006%, and Remainder Fe was acquired with weight percent. This raw material coarse powder was pulverized on the same conditions as an example 2. The

average grain size of the obtained fines was coarse compared with 5.1 micrometers and the case of an example 1. The process of henceforth, such as shaping, sintering, heat treatment, and corrosion-resistant evaluation, was also performed on the same conditions as an example 2. When the presentation of a sintered compact was analyzed, the analysis value of Nd 19.5%, Pr 6.5%, Dy 5.5%, B 1.0%, Nb 0.5%, aluminum 0.2%, Co 2.0%, Ga 0.10%, O 0.42%, C 0.06%, N 0.007%, and Remainder Fe was acquired. As for the sum of the area of the main phase crystal grain 10 micrometers or less, the diameter of crystal grain to the gross area of the magnet main phase crystal of this sintered compact was [ the diameter of crystal grain of the sum of the area of the main phase crystal grain 13 micrometers or more ] 19% 65%. A metal texture photograph is shown in drawing 5 R> 5. When the magnetic properties of this permanent magnet were evaluated, as shown in Table 2, it was a good value almost equivalent to the value of an example 2. Moreover, although, as for the corrosion resistance of this permanent magnet, it turned out that abnormalities are not accepted in nickel plating but it is in the level which is practically completely satisfactory even if 700 hours passed, as shown in Table 2, few breaks away occurred in a part of nickel plating by the 1000 passage of time, and it became clear that it was inferior to corrosion resistance in the comparison with the permanent magnet manufactured in the example 2.

[0025]

[Table 2]

|          | 焼結体分析値(wt%)  |      |      |       | 磁 气 特 性    |              |                   | 主相結晶粒の<br>総面積に対する<br>特定寸法の主相<br>結晶粒の面積の<br>和の割合(%)<br>≥10μ<br>≥13μ | 耐蝕性の<br>評価結果  |
|----------|--------------|------|------|-------|------------|--------------|-------------------|--|---|
|          | Nd+Pr<br>+Dy | O    | C    | N     | Br<br>(kG) | iHc<br>(kOe) | (BH)max<br>(MGoe) |  |   |
| 実施例<br>1 | 32.0         | 0.55 | 0.07 | 0.012 | 13.1       | 16.0         | 41.2              | 94   | 3<br>2000hr経過で<br>Niメッキに異常<br>なし  |
| 〃 2      | 31.5         | 0.48 | 0.06 | 0.008 | 12.8       | 24.5         | 39.4              | 90   | 6<br>2000hr ノ   |
| 〃 3      | 32.5         | 0.35 | 0.07 | 0.025 | 13.1       | 15.5         | 40.9              | 88   | 7<br>2000hr ノ   |
| 比較例<br>1 | 32.0         | 0.51 | 0.06 | 0.015 | 12.9       | 15.4         | 39.7              | 77   | 14<br>1000hr経過で<br>Niメッキに異常<br>なし<br>1500hr経過で<br>Niメッキに<br>わずかなハクリ<br>が発生  |
| 〃 2      | 31.5         | 0.42 | 0.06 | 0.007 | 12.8       | 23.7         | 39.2              | 65   | 19<br>700hr経過で<br>Niメッキに異常<br>なし<br>1000hr経過で<br>Niメッキの一部<br>わずかなハクリ<br>が発生 |

[Effect of the Invention] The R-Fe-B system sintering mold permanent magnet which has the corrosion resistance which was excellent with this invention, without reducing magnetic properties is obtained.

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[Translation done.]

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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The diameter of crystal grain to the gross area of the magnet main phase crystal is drawing having shown the relation of a between [ transient ] until HAKURI initiation of nickel plating of the diameter [ comparatively as opposed to the gross area of the magnet main phase crystal ] of crystal grain of the sum of the area of the main phase crystal grain 10 micrometers or less by the accelerated test of comparatively corrosion-resistant of the sum of the area of crystal grain with a main phase of 13 micrometers or more arises.

[Drawing 2] It is the metal texture photograph of the cross section of the thin band-like alloy produced by the strip cast method.

[Drawing 3] It is the metal texture photograph of the cross section after heat-treating the thin band-like alloy produced by the strip cast method at 1000 degrees C.

[Drawing 4] The diameter of crystal grain to the gross area of the magnet main phase is the metal texture photograph of the sintering mold permanent magnet whose sum of the area of the main phase crystal grain 13 micrometers or more 90% and the diameter of crystal grain is 6% for the sum of the area of the main phase crystal grain 10 micrometers or less.

[Drawing 5] For the sum of the area of the main phase crystal grain 10 micrometers or less, the diameter of crystal grain is [ the diameter of crystal grain to the gross area of the magnet main phase / the sum of the area of the main phase crystal grain 13 micrometers or more ] the metal texture photograph of 19% of sintering mold permanent magnet 65%.

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[Translation done.]

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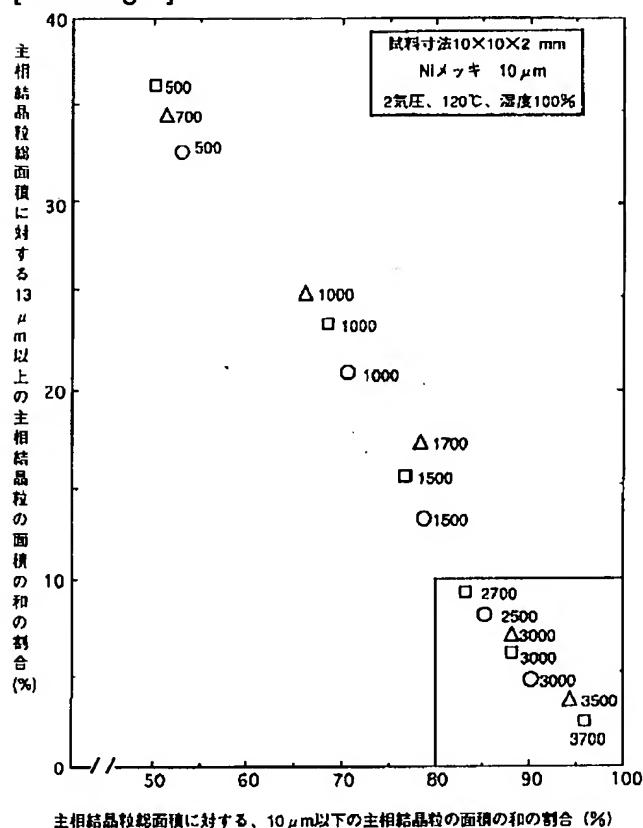
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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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## DRAWINGS

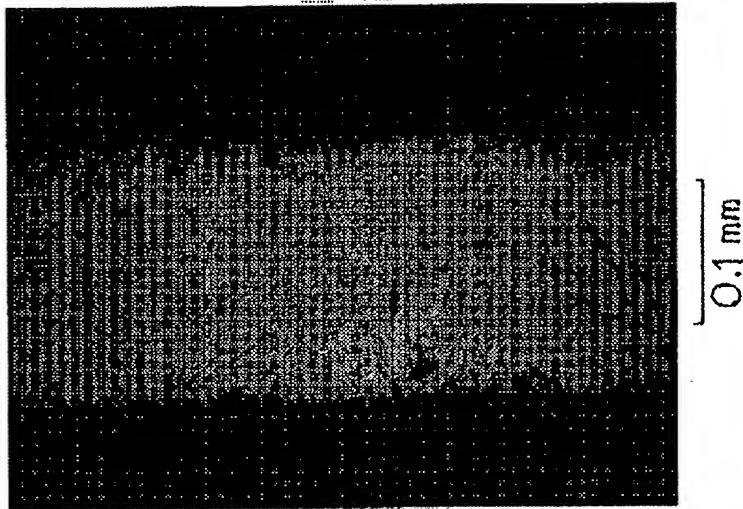
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[Drawing 1]



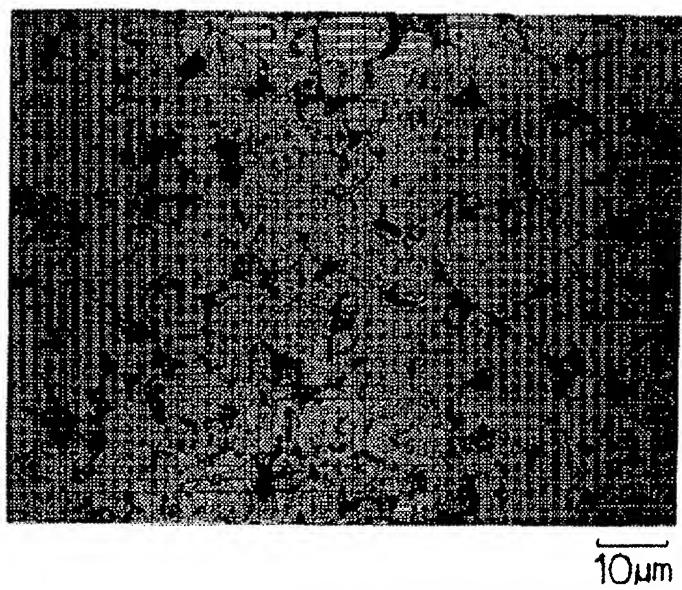
[Drawing 2]

図面代用写真



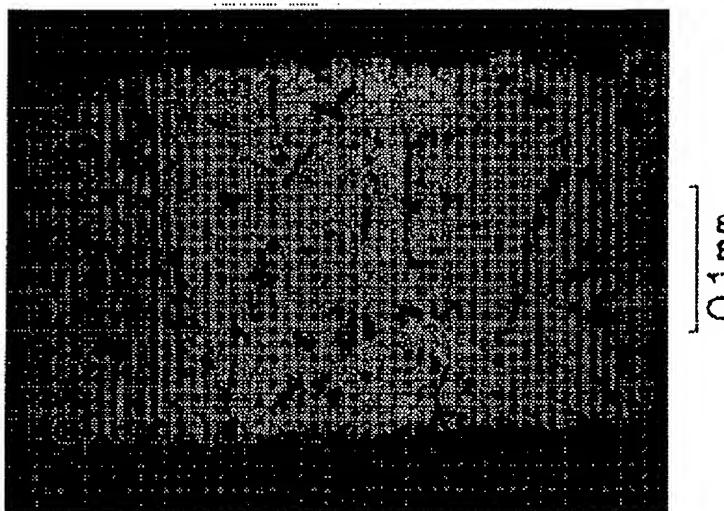
[Drawing 4]

図面代用写真



[Drawing 3]

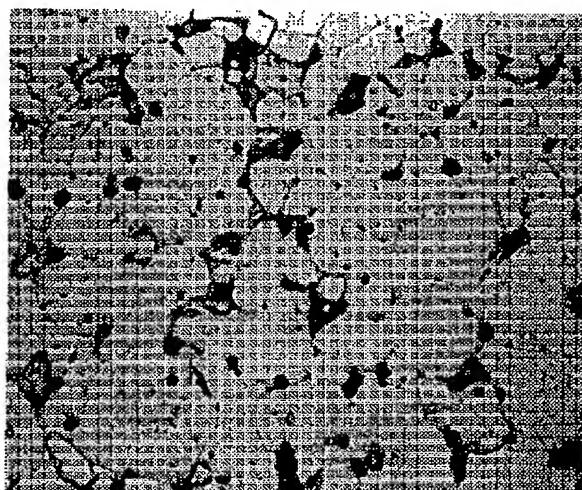
図面代用写真



写 真

[Drawing 5]

図面代用写真



10 μm

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[Translation done.]